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Multi-specific calibration of the B isotope proxy in calcareous red algae for pH reconstruction

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Calcareous red algae have calcified cell walls constituted by high-Mg calcite or aragonite (Morse et al., 2006). They are considered suitable paleoclimate archives due to their worldwide distribution and their longevity through indeterminate growth (Kamenos et al., 2008). Boron isotopes ($\delta^{11}\text{B}$) measured in their calcified thallus are considered a pH proxy (Hemming and Hanson, 1992). In seawater, boron occurs as boric acid and borate ion. Both species are enriched in ^{11}B as pH increases, with boric acid characterized by an enrichment factor of 27‰ compared to borate. The boron isotope proxy theory states that borate is exclusively incorporated in the mineral lattice (Hemming and Hanson, 1992). Therefore, if we measure $\delta^{11}\text{B}$ in carbonates, we can derive the seawater pH at the time of precipitation. Literature data on $\delta^{11}\text{B}$ in calcareous red algae are sparse, and the mechanisms of boron incorporation are still poorly known (Piazza et al., 2022). We tested the boron isotope-pH proxy on calcareous red algae grown at 1 m depth close to CO_2 seeps off the coasts of Ischia (Italy), and Methana (Greece), which are both characterized by a broad range of natural pH in seawater (from 6.80 ± 0.43 to 8.08 ± 0.07 units). Environmental data

characterizing the seawater during the algal growth were extracted from CMEMS products (Marine Copernicus Service Information), or provided by literature. The $\delta^{11}\text{B}$ values in the algae ($\delta^{11}\text{B}_{\text{algae}}$) analysed by Multi Collector Inductively-Coupled Plasma Mass Spectrometry ranged from 22.23‰ to 26.59‰, calibrated over a range of $\delta^{11}\text{B}$ in aqueous borate ($\delta^{11}\text{B}_{\text{borate}}$) extending from 12.68‰ to 18.05‰. A crystallographic control over boron incorporation was shown by the difference in the isotopic composition of carbonate polymorphs, with Mg-calcite enriched in ^{11}B compared to aragonite. Values of $\delta^{11}\text{B}_{\text{algae}}$ higher than $\delta^{11}\text{B}_{\text{borate}}$ could be attributed to the up-regulation of the calcifying fluid pH exerted by the algae. We proposed a multi-specific calibration using literature data of boron isotopes in cultured coralline algae combined with our new data on wild-grown specimens, widening the range of pH considered for $\delta^{11}\text{B}$ calibrations so far. The proposed calibration is particularly useful when experimental calibration is not possible, such as in the fossil record and in the case of ambiguous identifications.

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